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Contractor: Tulane University

Contract No.: DA18-108-AMC-186A

TITLE: SYNTHESIS OF SELECTED OXIDANTS

FINAL COMPREHENSIVE REPORT

Covering the Period

July 1, 1964 - July 1, 1966

SUBTITLE: Reactions of Manganese Compounds with Dinitrogen Pentoxide.

Prepared by

Hans B. Jonassen and Colin Hewlett

Date: July 1, 1966

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ABSTRACT

During the period of this contract the following phases were investigated:

1. a. Stability of chromyl nitrate by various additives
   b. Stability of chromyl nitrate under high nitrogen pressure.

2. Preparation of $CrO(NO_3)_2 \cdot 8H_2O$.

3. Estimated heats of formation and heats of reaction of some metal oxynitrates and perchlorates.

4. The decomposition products of chromyl nitrate were determined by mass spectroscopic analysis.

5. The reactions of $MnCl_2$, MnF_2, Mn acetyl-acetonate$_2$, $Mn_2O(NO_3)_2$, MnO_2 with N_2O_5 were investigated.

6. Reaction of potassium manganese(IV) hexafluoride with dinitrogen pentoxide.
   Reaction of potassium manganese(IV) hexafluoride with dinitrogen tetroxide.
   Reaction of potassium manganese(IV) hexachloride with dinitrogen tetroxide.
   Reaction of potassium manganese(III)hexacyanide with dinitrogen tetroxide.

7. Reactions of $MnCl_3$ with N_2O_4 and N_2O_5.

8. ~~Preparation of tetra alkyl ammonium = Mn_2Cl_4.~~

9. Preparation of Mn_2NOPh and $MnCl_3PhPO_3$.

10. Reaction of $MnCl_2(Ph_3PO)_2$ with N_2O_4.

11. Reaction of $MnCl_3(Ph_3PO)_3$ with N_2O_4.

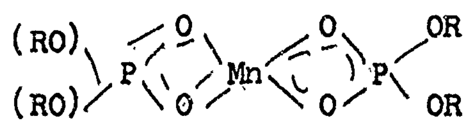
12. Reaction of $(NMe_4)_2[Mn_2Cl_4]$ with N_2O_4.

13. Reaction of $(NMe_4)_2[Mn_2Cl_4]Cl$ with N_2O_4.

14. Reaction of $(NMe_4)_2[Mn_2Cl_4]Cl_4$ with N_2O_4, in nitromethane.

ABSTRACT (contd).

15. Synthesis of:



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I N D E X

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FINAL COMPREHENSIVE REPORT

CONTRACT NO.: DA18-108-AMC-186A

REACTIONS OF MANGANESE COMPOUNDS WITH DINITROGEN PENTOXIDE

Prepared by: Hans B. Jonassen and Colin Hewlett

INTRODUCTION

The aim of this investigation was to prepare nitrato complexes of manganese in its higher oxidation states. The potential of such compounds as powerful oxidants was discussed in a previous report.

A review of nitrato complexes with special reference to those of manganese is presented here. Particular emphasis is placed on the infrared spectra of these compounds since they provide important structural information.

A brief review of the compounds of manganese in its higher oxidation states is followed by a description of experiments carried out in order to prepare such compounds.

Experiments designed to yield the required nitrato complexes are discussed and finally a novel reaction of manganese salts with trialkyl phosphates, analogous to the Arbuzov reaction, is described.

NITRATO COMPLEXES

Nitrato complexes have been prepared by a variety of methods. The reaction of metal chlorides or oxides with dinitrogen tetroxide or dinitrogen pentoxide are the most commonly used methods.

The nitrato group can be bonded to the metal in a unidentate or bidentate fashion. These structures can be distinguished from one another by means of infrared spectroscopy. The assignment of bonds for the unidentate nitrato group has long been established but the assignment of bond for the bidentate nitrato group has been achieved only recently[1] as no authentic bidentate nitrato complex was

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1) Addison and Simpson, J.Chem.Soc., 1965, 598.

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available.

The following table gives the assignments and approximate frequencies for both the unidentate and bidentate nitrato groups:

	Unidentate	Bidentate
NO_2 Sym. Stretch	ν_1 (1290) cm^{-1}	ν_2 (985)
NO Stretch	ν_2 (1000)	ν_1 (1630)
NO_2 Sym. bond	ν_3 (740)	ν_3 (785)
NO_2 Asym. Stretch	ν_4 (1480-1550)	ν_4 (1250)
NO_2 Asym. bond	ν_5 (715)	ν_5 (750)
Out of plane rocking	ν_6 (800)	ν_6 (700)

The bidentate frequencies were assigned for $Ti(NO_3)_4$ whose structure was shown by X-ray diffraction to include a bidentate nitrato group.

PROPERTIES

Bidentate nitrato groups are associated with strong oxidizing properties.[2] The nitrates of titanium, zirconium,

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2) Addison, Garner, Simpson, Sutton and Wallwork, Proc.Chem. Soc., 1964, 367.

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beryllium, copper(II), and tin(IV) all show these properties. That the nitrato group has to be bonded in a bidentate fashion for strong oxidizing properties to be observed was established by comparing the two nitrates, $Sn(NO_3)_4$ and $Sn(NO_3)_4$.2 pyridine. The latter is unreactive.

Addison[2] suggests that the bonding in bidentate nitrates is not through two bonds but that a 3-center bond may be involved.

NITRATO COMPLEXES OF MANGANESE

Anhydrous manganese nitrate contains unidentate nitrato groups, the highest infrared bond appearing at 1553 cm^{-1}.

The compound $Mn(Co)_5(NO_3)$ was prepared by the reaction of $Mn_2(Co)_{10}$ with dinitrogen tetroxide, and is important in that it provided an authentic unidentate nitrato complex and enabled the assignment of the infrared bonds of such a group. The anion $[Mn(NO_3)_4]^-$ was prepared by the reaction:[3]

$$MnCl_2 + 2Ph_3AsMeI + 4AgNO_3 \xrightarrow{MeCN} [Ph_3AsMe]_2\,[Mn(NO_3)_4]$$

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3) Straub, Drago and Donaghue, Inorg.Chem., 1, 848, 1962.

Infrared spectra and reflectance spectra both suggest unidentate bonding and hence 4-coordinate Mn^{II}. Mn^{II} can be tetrahedral as in the compounds $MnBr_4^{=}$ and $MnCl_2 \cdot 2Ph_3PO$.[4]

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4) Goodgame and Cotton, J.Chem.Soc., 1961, 3735.

MANGANESE in VALENCE STATES GREATER THAN II

The higher oxidation states of manganese are relatively unstable; they can be stabilized by ligands with highly electronegative donations, Cl^-, F^-, and best of all $O^{=}$. With less electronegative donors, the ligand is oxidized by transfer of charge to the metal atom.

PREPARATION OF $MnCl_3$

A number of preparations are described in the literature. All but one of these proved to be unsatisfactory.

1. Reaction of manganous chloride with chlorine[5] is

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5) Nickles, Compt. rend. 60, 480.

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reported to give $MnCl_3$. Anhydrous chlorine gas was bubbled into a suspension or solution of manganous chloride in the following solvents:

a. Carbon tetrachloride(suspension) - no reaction up to reflux temperature.
b. Nitromethane(suspension) - no reaction from -30° up to +30°.
c. Acetonitrile(suspension) - no reaction from -30° up to +30°.

d. Dimethyl Sulfoxide (solution) - explosive reaction with solvent.

e. Diethyl ether (suspension) - no reaction from -78° up to -20°. Explosion on warming to room temperature.

f. Ethanol (solution) - as for (e).

g. Methanol (solution) - smooth reaction at room temperature to give violet solution; removal of excess chlorine reverses the reaction giving manganous chloride.

(ii) The reaction of manganese dioxide with acetyl chloride is reported to give $Mn^{IV}Cl_4$. Very slight reaction over two days giving a violet solution, but no product could be isolated.

(iii) The reaction of anhydrous hydrogen chloride with a suspension of manganese dioxide in carbon tetrachloride or ether is reported to give $Mn^{IV}Cl_4$.[6]

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6) Nouveau Traite de Chimie Miner ale. XVI., 971.

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and $Mn^{III}Cl_3$.[7]

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7) Gile, Chemistry and Industry, 1961, 989.

This reaction proceeds smoothly at -25°C, less than 10% of the manganese dioxide reacts, and the product is obtained as a green viscous oil, solidifying to a glass at -78°. It is soluble in nitromethane and ether, insoluble in carbon tetrachloride. It decomposes at room temperature. The compound was used without further purification as a starting material for attempted preparation of nitrato complexes. (see next section).

CHLORO-COMPLEXES OF MANGANESE

The chloro-complexes K_2MnCl_6 and K_2MnF_6 proved to be unsuitable starting materials (next section) owing to their insolubility and tendency to decompose spontaneously. The tetramethylammonium salt of $[Mn^{IV}Cl_6]^{=}$ was described in a recent publication[8] and that of $[Mn^{III}Cl_5]^{=}$ reported without analytical data.[7]

8) Moews, Inorg.Chem., 5, 5, 1966.

These preparations were repeated. No preparative details were given by Gill, but a product was obtained by addition of solid NMe_4Cl to a solution of $MnCl_3$ in nitromethane at -20°C. Evaporation of the solvent, after filtration, gave a brown powder. Moew's preparation yielded a bright yellow solid soluble in acetonitrile.

Preparation of the Mn(II) salt, $(NMe_4)_2MnCl_4$, was attempted by reaction of NMe_4Cl with $MnCl_2$ in aqueous ethanol and acetone mixture.

The analytical data obtained for these products failed to fit the simple structure shown above, and it is necessary to postulate dimeric structure in order to rationalize the analyses. A basic structural unit $[Mn_2Cl_4]$ which remains intact throughout the analysis for halide is common to all three compounds. Compounds 1, 2 and 3 are shown below; compound 1. resulted from the $Mn(II)Cl_2$ experiment, compound 2. from the $Mn^{III}Cl_3$ experiment, and compound 3. from the reaction of $[Mn^{VII}O_4]^-$ with HCl.

1. $(NMe_4)_2[Mn_2Cl_4]^{=}$

Calculated C 24.0, H 6.0, N 7.0, available Cl, 0.0.

Found C 24.0, H 6.2, N 6.3 " Cl, 0.0.

2. $(NMe_4Cl\cdot[NMe_4][Mn_2Cl_4])$

Calculated C 22.1, H 5.5, N 6.4, available Cl, 8.2.

Found C 22.4, H 5.7, N 5.8, " " 9.4

3. $(NMe_4)_2[Mn_2Cl_4]^{++}4Cl^-$ $(NMn_4Cl)_2\cdot[Mn_2Cl_4]Cl_2$

Calculated C 17.7, H 4.45, N 5.2, available Cl 26.2

Found C 18.0, H 4.6, N 4.5, " Cl 26.6

The infrared spectra of these compounds show only the bands associated with NMe_4^+. The presence of chloride ions is shown by reaction with dinitrogen tetroxide, the product of which show ionic as well as covalent nitrate groups (see next section).

These suggested structures are unusual since they involve manganese in low as well as high valence states; thus compound 1 will contain Mn° as well as Mn^{+2}; compound 2, Mn° as well as Mn^{3+}, and compound 3, Mn° as well as Mn^{+8} or Mn^{+2} and Mn^{+3} or Mn^{+3} and Mn^{+3}.

Manganese does form dimers, often containing a metal-metal bond. Manganese dimer with the metal in more than one valence state are also known.[8] (e.g. $[Mn(dipy)_{2}O]_2^{3+}$,

8) Nyholm and Turco, Chemistry and Industry, 74, 1960.

containing Mn^{+3} and Mn^{+4}).[8]

TRIPHENYLPHOSPHINE OXIDE COMPLEXES OF MANGANESE

A. Manganese in +2 oxidation state.

Both manganous chloride and manganous nitrate react with triphenyl phosphine oxide in ethanol to give the complexes MnX_2L_2.[10] A tetrahedral structure was assigned

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10) Goodgame and Cotton, J.Chem.Soc., 3735, 1961.

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to the chloride from a study of the reflectance spectrum. These preparations were repeated.

$MnCl_2(Ph_3PO)_2$

Calculated	C 63.3	H 4.4	P 9.1	Cl 10.4%
Found	C 62.8, 63.3	H 4.4	P 9.1	Cl 10.5%

$Mn(NO_3)_2(Ph_3PO)_2$

Calculated	C 58.7	H 4.1	P 9.7	N 3.8%
Found	C 56.8	H 4.2	P 7.9	N 3.6%

The chloride was converted to the nitrate by reaction with dinitrogen tetroxide in nitromethane or acetonitrile at room temperature. The reaction proceeded smoothly, no side reaction such as substitution on the phenyl groups being observed. $Mn(NO_3)_2(Ph_3PO)_2$, Found, C 59.8, H, 4.45, N, 3.75, P, 8.65%

B. Manganese in +3 oxidation state.

Manganic chloride was stabilized by complexing with triphenylphosphine oxide. Addition of triphenyl phosphine oxide to a solution of manganic chloride in nitromethane did not yield the desired product, but by carrying out the preparation of $MnCl_3$ in the presence of Ph_3PO, a blue crystalline product was obtained which could be recrystallized from ethyl acetate without decomposition. It liberated iodine from an acid solution of potassium iodide, showing the manganese to be in an oxidation state greater than II.

$MnCl_3 \cdot 3(Ph_3PO)$

Calculated	C 65.2,	H 4.5,	P 9.4,	Cl 10.6%
Found	C 64.6,	H 4.4,	P 9.7	Cl 11.1%

ATTEMPTED PREPARATION OF NITRATE COMPLEXES

1. Reaction of K_2MnF_6 with N_2O_5 and N_2O_4. This was described in Seventh Quarterly Report.

   Heterogeneous reaction, product showing ionic nitrate groups only.

2. Reaction of K_2MnCl_6 with N_2O_5 and N_2O_4. This was described in Seventh Quarterly Report.

   Product shows ionic nitrate groups only.

3. Reaction of MnO_2, K_2MnO_4, $KMnO_4$ with N_2O_4 in nitramethane.

   No reaction up to +70°C.

4. Reaction of $MnCl_2$ with N_2O_4 in nitromethane.

   Crude manganic chloride was used in nitromethane solution. Reaction at -20° gave no product. Reaction at room temperature gave small yield of hygroscopic colorless solid whose infrared spectrum showed bands at 1690 cm^{-1} and 1580 cm^{-1} suggesting both unidentate and bidentate nitrato groups.

5. Reaction of $MnCl_2(Ph3PO)_2$ with N_2O_4 in either nitromethane or acetonitrile gave $Mn(NO_3)_2(Ph_3PO)_2$ (see previous section). Reaction would not proceed in ethyl acetate solution.

6. Reaction of $MnCl_3(Ph_3PO)_3$ with N_2O_4 in nitromethane gave infrared bands at 1690 cm^{-1}, 1560 cm^{-1}, 1340 (broad), and 1020 cm^{-1}. The high frequency absorption at 1090 cm^{-1} suggests bidentate bonding, but the broad peak at 1340 suggests that ionic groups are also present. Products decomposed in attempts to recrystallize in the usual solvents.

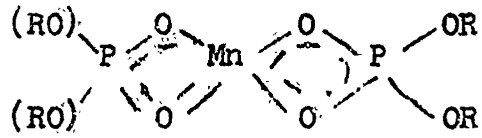
7. Reaction of $(NMe_4)_2[Mn_2Cl_4]$ with N_2O_4 in nitromethane gave a yellow solid whose infrared spectrum shows bands at 1610 cm^{-1}, 1370 cm^{-1}, and 820 cm^{-1}, suggesting bidentate covalent nitrate groups as well as ionic nitrate groups. Products could not be recrystallized without decomposition in the usual solvents.

8. Reaction of $(NMe_4)_2[Mn_2Cl_4]Cl$ with N_2O_4 in nitromethane gave a product whose infrared spectrum shows band at 1630 cm^{-1}, 1540 cm^{-1}, 1370 cm^{-1}, 1025 cm^{-1} and 815 cm^{-1} suggesting both unidentate and bidentate covalent nitrate groups as well as ionic nitrate groups. Rapid decomposition of products when recrystallization was attempted in the usual solvents.

9. Reaction of $(NMe_4)_2[Mn_2Cl_4]Cl_4$ with N_2O_4 in nitromethane or acetonitrile gave a yellow solid whose infrared spectrum gave bands at 1550 cm^{-1}, 1370 cm^{-1}, 812 cm^{-1}, suggesting unidentate nitrato groups as well as ionic nitrate groups. Violent decomposition when attempts were made to recrystallize in the usual solvents.

REACTION OF TRIALKYL PHOSPHATE WITH $MnCl_2$

Both triethyl and trimethyl phosphates (abbrev. TEP, TMP) form hygroscopic complexes of the type $MnCl_2 \cdot 2L$ with manganous chloride in ethanol at room temperature. If the solution is heated to the boiling point, elimination of alkyl halide takes place with the formation of the complex.



This alkyl halide elimination is analagous to the Arbuzov reaction.

$MnCl_2$ also reacts with a nitromethane solution of TMP or TEP at the boiling point to give this complex in a heterogeneous reaction.

$MnCl_2$ reacts with TEP in the absence of solvent at 120° to give the complex.

$Mn(NO_3)_2$ reacts with TMP at 170° to give the same compound.

SUMMARY

The results of this study indicate the great difficulty in the synthesis of manganese nitrato complexes where the manganese is in a high oxidation state and the nitrato group coordinates as a bidentate group. Both of these conditions are necessary to produce in a complex the required powerful oxidizer quality.

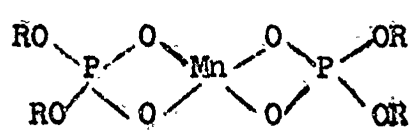
Several significant results however were obtained which should be followed up.

1. The chloro complex of the type [Mn_2Cl_4] which seems to contain a metal metal bond [Mn-Mn] involving manganese in different oxidation states ($0 \rightarrow +6$). This is an area of great interest at the present time.[8]

2. The interaction of these complexes with N_2O_4 seems to produce new complexes containing bidentate nitrato groups which seem to have oxidizing properties especially for those where one of the manganese is in a high oxidation state.

Attempts to prevent the decomposition of these complexes or recrystallization should be carried out with high oxygen content solvents.

3. The synthesis of complexes of the type ($R=CH_3, C_2H_5$)



is an interesting development of this study and work is being continued in this area.